



(11) Application No. **AU 2004269169 B2**

(19) AUSTRALIAN PATENT OFFICE

(54) Title
Fuel compositions comprising Fischer-Tropsch derived fuel

(51)⁶ International Patent Classification(s)
C10L 1/08 (2006.01) 2BMEP C10L
C10L 1/16 (2006.01) 1/16
C10L 1/08 20060101ALN200510
20060101AFI2006072 08BMEP
PCT/EP2004/052014

(21) Application No: 2004269169

(22) Application Date: 2004 .09 .02

(87) WIPO No: W005/021688

(30) Priority Data

(31) Number	(32) Date	(33) Country
03255506.2	2003 .09 .03	EP

(43) Publication Date: 2005 .03 .10

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(56) Related Art
See reference of WO 2005/021688

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
10 March 2005 (10.03.2005)

PCT

(10) International Publication Number
WO 2005/021688 A1

- (51) International Patent Classification: C10L 1/04, 1/08 (81) Designated States (unless otherwise indicated, for every kind of national protection available): AT, AG, AI, AM, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GH, GM, GR, HT, HU, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SF, SG, SK, SL, SY, TI, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (21) International Application Number: PCT/EP2004/052014 (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (22) International Filing Date: 2 September 2004 (02.09.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 03255506.2 3 September 2003 (03.09.2003) EP
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- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/021688 A1

(54) Title: FUEL COMPOSITIONS COMPRISING FISCHER-TROPSCH DERIVED FUEL

(57) Abstract: Use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of reducing the amount of additives, in particular antifoaming and/or dehazing additives, in the composition. The Fischer-Tropsch fuel may be used to reduce the amount of silicon containing additives in the composition, or generally to reduce silicon levels, and in turn to reduce loss of efficiency of fuel atomisation and/or combustion in a fuel consuming system which is running on the fuel composition, and/or to reduce build up of deposits, in particular silicon deposits, in such a system. The Fischer-Tropsch derived fuel is preferably a gas oil and the fuel composition suitably a diesel fuel composition.

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Fuel compositions

The present invention relates to fuel compositions, in particular automotive fuel compositions such as diesel fuel compositions, and to their preparation and their uses, as well as to the use of certain types of fuel in fuel compositions for new purposes.

Typical diesel fuels comprise liquid hydrocarbon middle distillate fuel oils having boiling points from about 150 to 400 °C. Examples of such fuels include the reaction products of Fischer-Tropsch methane condensation processes, for example the process known as Shell Middle Distillate Synthesis (van der Burgt et al, "The Shell Middle Distillate Synthesis Process", paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985; see also the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK). These Fischer-Tropsch derived gas oils are low in undesirable fuel components such as sulphur, nitrogen and aromatics and tend to reduce vehicle emissions when used as automotive fuels in blends with other diesel fuels such as petroleum derived gas oils.

Diesel fuel compositions for use in typical current diesel (compression ignition) engines tend to include one or more additives to enhance their performance and properties. Examples of such additives include detergents, which can help to reduce and/or remove combustion related engine deposits; antifoaming agents to reduce foaming during engine refuelling; and dehazers, which help remove suspended water from the fuel.

In some contexts, however, it may be desirable to reduce the levels of such additives in fuel compositions.

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This may be driven by consumer preferences and/or by technical or economic considerations.

The antifoaming agents typically preferred for use in automotive fuels are silicone based. Silicon has now
5 been found in the deposits which accumulate in the fuel injectors of diesel engines. Since excessive deposits in these injectors can impair fuel atomisation and combustion and hence overall engine efficiency, it is desirable to reduce the use of any material which might
10 contribute to deposit formation. Thus, although there is no definite link between the use of antifoaming additives and nozzle fouling, the risk of potential problems might be reduced if antifoaming performance could be improved in alternative ways.

15 Moreover, although silicon free antifoaming agents are known, they tend to perform poorly when used in fuel compositions containing detergent additives, and can therefore be unsuitable for use in typical commercial diesel fuel compositions.

20 It might therefore be desirable to provide fuel compositions, in particular diesel fuel compositions, having lower levels of or preferably no silicon containing additives, without undue loss of antifoaming performance and without undue effect on other fuel
25 properties such as for example dehazing and detergency performance. It may also be desirable to provide fuel compositions containing lower levels of additives generally, in particular antifoaming, dehazing and/or detergent agents.

30 The present inventors have now found that certain fuel components can be used to replace, entirely or at least partially, such additives in fuel compositions, the components themselves having antifoaming, dehazing and/or

detergency properties both alone and when blended with other fuel components.

In its first, broadest aspect, the present invention provides the use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of reducing the amount of additives (or additives other than detergent additives) in the composition. In other words, the Fischer-Tropsch derived fuel may be used at least partly in place of additives which would otherwise have been present in the composition, suitably by performing at least part of the usual and/or intended function of those additives.

According to a second aspect of the invention there is provided use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of reducing the amount of silicon in the composition.

According to a third aspect of the invention there is provided use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of improving the antifoaming and/or dehazing properties of the composition.

According to a fourth aspect of the invention there is provided a fuel composition comprising either:

(i) a Fischer-Tropsch derived fuel and a silicon free or substantially silicon free antifoaming additive, optionally together with one or more other fuel components, wherein the amount of said antifoaming additive present is less than a fuel composition without said Fischer-Tropsch derived fuel, the composition preferably being free of detergent additives; or

(ii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of antifoaming additives and/or of silicon containing antifoaming additives and/or of dehazing additives, and is preferably also free of detergent additives and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel; or

(iii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of dehazing additives and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel; or

(iv) a Fischer-Tropsch derived fuel and one or more non-detergent fuel additives, optionally together with one or more other fuel components, wherein the composition is free of or substantially free of silicon and substantially free of antifoaming additive and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel.

In particular, the Fischer-Tropsch derived fuel may be used for the purpose of reducing the amount of antifoaming and/or dehazing additives in the composition. It may be used so as to reduce the amount of silicon containing additives (especially silicon containing antifoaming additives). It is preferably also used to reduce the amount of detergent additives.

According to a fifth aspect of the invention there is provided a process for the preparation of a fuel composition, which process comprises blending either:

- 5 (i) a Fischer-Tropsch derived fuel and a silicon free or substantially silicon free antifoaming additive, optionally together with one or more other fuel components, the composition preferably being free of detergent additives; or
- (ii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of antifoaming additives and/or of silicon containing antifoaming additives and/or of dehazing additives, and is preferably also free of detergent additives; or
- 10 (iii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of dehazing additives; or
- (iv) a Fischer-Tropsch derived fuel and one or more non-detergent fuel additives, optionally together with one or more other fuel components, wherein the composition is free of or
- 15 substantially free of silicon;

wherein said Fischer-Tropsch fuel is blended for the purpose of reducing the amount of additives (other than detergent additives) in the fuel composition, or for the purpose of reducing the amount of silicon in the fuel composition or for the purpose of improving the antifoaming and/or dehazing properties of the composition.

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that would otherwise have been excluded due to their interactions with other components of the composition.

Additives which the fuel composition might contain less of, or even none of, as a result of using the Fischer-Tropsch derived fuel in it include for example lubricity enhancers, ignition improvers, anti-rust agents, corrosion inhibitors, reodorants, anti-wear additives, anti-oxidants, metal deactivators, anti-static agents, pipeline drag reducers, flow improvers, wax anti-settling agents and mixtures thereof.

The Fischer-Tropsch derived fuel is preferably a gas oil, although in some contexts it may be a Fischer-Tropsch derived naphtha or kerosene fuel. The fuel composition is preferably an automotive fuel composition, more preferably for use in an internal combustion engine, and most preferably it is a diesel fuel composition.

In the context of the present invention, "use" of a Fischer-Tropsch derived fuel in a fuel composition means incorporating the Fischer-Tropsch fuel into the composition, typically as a blend (ie, a physical mixture) with one or more other fuel components and/or fuel additives, conveniently before the composition is introduced into an internal combustion engine or other system which is to be run on the fuel composition. "Use" also embraces using the Fischer-Tropsch derived fuel on its own as a fuel composition.

In the present context the term "reducing" embraces reduction to zero; in other words, the Fischer-Tropsch derived fuel may be used to replace the relevant material(s) either partially or completely. The reduction may be as compared to the level of the relevant additive(s) which would otherwise have been incorporated into the fuel composition in order to achieve the

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properties and performance required and/or desired of it in the context of its intended use. This may for instance be the level of the additive(s) which were present in the fuel composition prior to the realisation that a Fischer-Tropsch derived fuel could be used in the way provided by the present invention, and/or which were present in an otherwise analogous fuel composition intended (eg, marketed) for use in an analogous context, prior to increasing the amount of the Fischer-Tropsch derived fuel that it contained.

In the case for example of a fuel composition intended for use in an automotive engine, certain minimum antifoaming, dehazing and/or detergency properties may be desirable in order for the composition to meet current fuel specifications, and/or to safeguard engine performance, and/or to satisfy consumer demand. The present invention makes it possible to use a Fischer-Tropsch derived fuel at least partly in place of the additive(s) that would otherwise be needed to achieve such properties.

Thus, in the context of reducing the level of an additive which has a particular effect on the properties or performance of the overall fuel composition, the Fischer-Tropsch derived fuel may be used to itself achieve at least part of that effect instead of the additive. The resultant composition can contain a lower level of the additive but without loss of, or without undue loss of, preferably even with an improvement in, the relevant desired properties or performance.

Preferably the Fischer-Tropsch derived fuel is used to reduce the w/w concentration of the relevant additive(s) in the fuel composition by at least 10 %, more preferably by at least 20 or 30 %, yet more

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preferably by at least 50 or 70 or 80 or even 90 %. It may, as described above, be used to replace the relevant additive(s) entirely, leaving a concentration of such additive(s) in the composition of 0 % w/w, ie, the fuel composition is free of the relevant additive(s).

It may for instance be used to replace antifoaming additive(s) to an extent that the concentration of antifoaming additives remaining in the fuel composition is 10 ppmw (parts per million by weight) or less, preferably less than 10 ppmw, more preferably 5 ppmw or less, yet more preferably less than 5 ppmw, still more preferably 4 or even 3 ppmw or less. Most preferably it may be used to replace antifoaming additive(s) substantially entirely, the fuel composition being nearly or essentially free of such additives and containing for example 2 ppmw or less, preferably 1 ppmw or less, more preferably 0.5 ppmw or less of antifoaming additives.

(All additive concentrations quoted in this specification refer, unless otherwise stated, to active matter concentrations.)

By "antifoaming additive" is meant a reagent, or a formulation containing such a reagent, which is suitable for inclusion in a fuel composition (in particular a diesel fuel composition) and which has the effect of improving the antifoaming properties of that composition for instance in the manner described below. Known silicone based antifoaming fuel additives include the polyether-modified polysiloxanes commercially available as TEGOPREN[™] 5851 (ex Goldschmidt), Q 25907 (ex Dow Corning), SAG[™] TP-325 (ex OSI) and RHODORSIL[™] (ex Rhone Poulenc). Known silicon free antifoaming additives include various alcohols, (poly)ethers and (poly)acrylates, such as Laurex[™] DF (ex A & W),

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HD-Ocenol™ 70/75 (ex Henkel), X702 (ex Mobil), Nalfloc™
71-D5 (ex Nalfloc) and Unem™ 4420 (ex Unichema).

Instead or in addition, the Fischer-Tropsch derived
fuel may be used to reduce the concentration of silicon
5 containing additives, in particular silicon containing
antifoaming additives, in the composition to 10 ppmw or
less, preferably 5 ppmw or less, more preferably 4 ppmw
or less, yet more preferably 3 or 2 ppmw or less. Again,
it is suitably used to replace such silicon containing
10 additives substantially entirely, the fuel composition
being nearly or essentially free of such additives and
containing for example 1 ppmw or less, preferably 0.8
ppmw or less, more preferably 0.5 or even 0.1 ppmw or
less of silicon containing additives. Most preferably
15 the fuel composition will contain no (ie, 0 % w/w)
silicon containing additives, in particular silicon
containing antifoaming additives.

As a result of using the Fischer-Tropsch derived
fuel in this way, the fuel composition ideally contains
20 1000 ppbw (parts per billion by weight) or less of
silicon, preferably 500 ppbw or less (ideally less), more
preferably 400 or 300 or 200 ppbw or less, yet more
preferably 100 or 50 or even 20 or 10 ppbw or less, most
preferably no silicon or at least only trace amounts
25 attributable to environmental contamination (dust).

The Fischer-Tropsch derived fuel may be used to
replace dehazing additive(s) to an extent that the
concentration of dehazing additives remaining in the fuel
composition is 15 ppmw or less, preferably 10 ppmw or
30 less, more preferably 5 ppmw or less. Most preferably it
may be used to replace dehazing additive(s) substantially
entirely, the fuel composition being nearly or
essentially free of such additives and containing for

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example 3 ppmw or less, preferably 2 ppmw or less, more preferably 1 or even 0.5 ppmw or less of dehazing additives.

By "dehazing additive" is meant a reagent, or a
5 formulation containing such a reagent, which is suitable for inclusion in a fuel composition (in particular a diesel fuel composition) and which has the effect of improving the dehazing performance of that composition for instance in the manner described below. Known
10 dehazing fuel additives include alkoxylated phenol formaldehyde polymers such as those commercially available as NALCO™ EC5462A (formerly 7D07) (ex Nalco) and TOLAN™ 2683 (ex Petrolite).

By "detergent additive" is meant a detergent, or a
15 formulation containing a detergent, suitable for inclusion in a fuel composition, in particular a diesel fuel composition. A detergent is an agent (suitably a surfactant) which can act to remove, and/or to prevent the build up of, combustion related deposits within a
20 fuel combustion system, in particular in the fuel injection system of an engine such as in the injector nozzles. Such materials are sometimes referred to as dispersant additives.

Examples of known detergents include polyolefin
25 substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or reaction products of amines and polyolefin (eg, polyisobutylene) maleic anhydrides.
30 Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Detergent-containing diesel fuel additives are known and

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commercially available for instance from Infineum (eg, F7661 and F7685), Octel (eg, OMA 4130D) and Lubrizol (eg, the Lz8043 series).

Where a diesel fuel composition includes a
5 detergent, typical concentrations lie in the range 20 to 500 ppmw active matter detergent based on the overall fuel composition, more preferably 40 to 500 ppmw, most preferably 40 to 300 ppmw or 100 to 300 ppmw or 150 to 300 ppmw. In the context of the present invention,
10 however, preferred concentrations may be 400 ppmw or less, more preferably 300 ppmw or less, yet more preferably 200 or 100 ppmw or less, most preferably 50 ppmw or 20 ppmw or less, such as from 10 to 100 ppmw or from 10 to 50 ppmw, active matter detergent based on the
15 overall fuel composition. Any detergent additives present are preferably incorporated at levels no higher than, preferably lower than, more preferably 0.8 times or less, yet more preferably 0.5 times or less, their standard recommended single treat rate(s). Still more
20 preferably, as described above, the fuel composition contains no detergents.

According to a second aspect of the present invention, there is provided the use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of
25 improving the antifoaming and/or dehazing properties of the composition, and preferably also for the purpose of improving the detergency properties of the composition. Again the improvement may be as compared to the relevant property(ies) of the fuel composition prior to the
30 realisation that a Fischer-Tropsch derived fuel could be used in the way provided by the present invention, and/or of an otherwise analogous fuel composition intended (eg, marketed) for use in an analogous context, prior to

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increasing the amount of the Fischer-Tropsch derived fuel that it contained.

Again the fuel composition is preferably an automotive fuel composition, typically for use in an internal combustion engine, and is more preferably a diesel fuel composition. The Fischer-Tropsch derived fuel is preferably a gas oil.

The antifoaming properties of a fuel composition may be assessed with reference to the volume of foam generated when a sample of the composition is filled into an appropriate vessel, and/or to the rate at which the thus generated foam dissipates. Standard test procedures may be used to assess such parameters, such as the Association Française de Normalisation (AFNOR) procedure NF M 07-075 and/or tests based on such procedures, for example the method used in Examples 1 and 2 below.

Thus, an improvement in antifoaming properties may be manifested by a reduction in foam volume, and/or a reduction in foam dissipation time or foam collapse time (which equates to an increase in foam dissipation rate), when the fuel composition is tested in this way. Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve a reduction in foam volume of at least 2 %, more preferably at least 4 %, yet more preferably at least 6 or 10 %, most preferably at least 12 or 15 or 20 %, even up to 22 or 25 % or more, of that generated under the same test conditions by the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or of that generated by the same fuel composition under the same test conditions prior to replacement, in accordance with the present invention, of some or all of its

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antifoaming or other additive(s) by the Fischer-Tropsch derived fuel.

Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve a reduction in foam dissipation time of at least 15 %, more preferably at least 18 %, most preferably at least 20 or 30 or 40 %, even up to 50 or 60 or 70 or 75 % or more, of that exhibited under the same test conditions by the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or of that exhibited by the same fuel composition under the same test conditions prior to replacement, in accordance with the invention, of some or all of its antifoaming or other additive(s) by the Fischer-Tropsch derived fuel.

Preferably it is used in an amount sufficient to achieve a foam volume of 105 ml or less, more preferably 100 ml or 90 ml or less, when a 100 ml sample of the resultant fuel composition is tested according to the Association Française de Normalisation (AFNOR) procedure NF M 07-075 or a test based on that procedures, for instance as in Examples 1 and 2 below. Preferably it is used in an amount sufficient to achieve, under the same test conditions, a foam dissipation time of 50 seconds or less, more preferably 40 or 35 seconds or less, yet more preferably 30 or 25 or 20 or 15 seconds or less.

The dehazing, or water shedding, properties of a fuel composition may be assessed by mixing a sample of the composition with an aqueous phase and observing the appearance of the resultant fuel and/or aqueous layers, and/or of their interface, after an appropriate settling period (for example 2 hours or more, preferably 3 or 4 or 5 hours or more). Poorer dehazing properties will be

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indicated in particular by a more "cloudy" fuel layer containing suspended moisture droplets and/or by a less distinct boundary between the two layers. They may also be indicated by a higher loss of the aqueous phase into the fuel layer if, after settling, the aqueous layer has reduced in volume compared to the volume originally added to the fuel sample (on occasions water can be absorbed into the fuel and yet not cause cloudiness, for instance if the fuel contains components such as certain oxygenates that help increase the miscibility of the fuel and aqueous phases).

Instead or in addition, dehazing properties may be assessed with reference to the water content of the resulting fuel layer for instance using a Karl Fischer or similar meter, again after an appropriate period of settling (for example 12 hours or more, preferably 24 hours or more). Standard test procedures may be used to assess such parameters, such as the ASTM procedure D1094 ("Water reaction of aviation fuels") or a version thereof modified for use with the particular fuel composition under test, such as for example the method used in Examples 4 to 6 below.

Thus, an improvement in dehazing properties may be manifested by an improvement (ie, less cloudiness) in the visual appearance of the settled fuel and/or aqueous layers and/or of their interface in a test of the type described above. It may instead or in addition be manifested by a reduction in the amount of water lost to the fuel layer, and/or by a reduction in the water content of the settled fuel layer.

Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve at least a noticeable improvement, more preferably at least a 30 % improvement,

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yet more preferably at least a 50 % or 75 % or 100 % improvement, in the visual appearance of the settled fuel and/or aqueous layers and/or of their interface, compared to that observed under the same test conditions for the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or to that observed for the same fuel composition under the same test conditions prior to replacement, in accordance with the present invention, of some or all of its dehazing or other additive(s) by the Fischer-Tropsch derived fuel.

Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve a reduction in fuel layer water content of at least 5 %, more preferably at least 9 or 10 %, most preferably at least 15 or 20 or 30 or 40 or 50 %, even up to 60 or 70 or 75 % or more, of that exhibited under the same test conditions by the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or of that exhibited by the same fuel composition under the same test conditions prior to replacement, in accordance with the present invention, of some or all of its dehazing or other additive(s) by the Fischer-Tropsch derived fuel.

Preferably it is used in an amount sufficient to achieve a fuel layer water content, after 24 hours' settling, when an 80 ml sample of the fuel composition is tested as described above with 20 ml of an aqueous buffer under ambient conditions, of 120 mg/kg or less, more preferably 110 or 100 mg/kg or less, yet more preferably 90 or 80 or 70 or 50 or 40 or 30 mg/kg or less.

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Preferably it is used in an amount sufficient to cause, under the same conditions, no visually detectable loss of the aqueous buffer into the fuel layer after 4 hours' settling.

5 For kerosene fuels an appropriate test of dehazing performance may be the Institute of Petroleum test method IP 452 ("Determination of water shedding properties (WASP) of aviation kerosene"). According to this method, the borderline for pass/fail is a residual water content
10 of ~500-600 mg/l, a lower value therefore indicating better performance. Preferably, in accordance with the present invention, the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve a residual water content when tested in this way which is at least 20 %
15 lower, more preferably at least 30 % lower, yet more preferably at least 40 or 50 or 60 % lower, than that achieved under the same test conditions by the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less
20 of), the Fischer-Tropsch derived fuel present, and/or of that exhibited by the same fuel composition under the same test conditions prior to replacement, in accordance with the present invention, of some or all of its dehazing or other additive(s) by the Fischer-Tropsch
25 derived fuel. Suitably it is used in an amount sufficient to achieve, under such test conditions, a residual water content of 500 mg/l or less, preferably of 400 or 350 mg/l or less, more preferably of 300 mg/l or less, yet more preferably of 250 or 200 or even 180 mg/l
30 or less.

The detergency properties of a fuel composition, or of a fuel additive in a fuel composition, may be assessed with reference to the effect of running a fuel combustion

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system (for example a diesel engine) using the composition, on the level of combustion related deposits in the system. Such deposits may accumulate for instance in the fuel injection system of an engine, causing fouling of the injector nozzles. Detergent effects may be manifested by a reduction in previously incurred nozzle fouling, when an engine is subsequently run on the relevant fuel composition; an improved detergency performance may therefore be manifested by a higher such reduction, when the engine is run for a given period of time on a fuel composition prepared according to the present invention, than when the same engine is run, for the same period of time and under the same conditions, on the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or on the same fuel composition prior to replacement, in accordance with the present invention, of some or all of its detergent or other additive(s) by the Fischer-Tropsch derived fuel.

An improvement in detergency performance may instead or in addition be manifested by a reduction in the rate of build up of subsequent fouling compared to that which would be incurred by running the engine, for the same period of time and under the same conditions, on the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably with 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or on the same fuel composition under the same test conditions prior to replacement, in accordance with the present invention, of some or all of its detergent or other additive(s) by the Fischer-Tropsch derived fuel.

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Degree of nozzle fouling may be assessed in a number of ways, for instance visually, by measuring the mass of deposits in a fouled nozzle or by measuring the fluid flow (for instance, fuel flow or more preferably air flow) properties of the fouled nozzle relative to those of the clean nozzle.

An appropriate test might for example determine the degree of nozzle fouling (conveniently in the form of a percentage injector fouling index) under steady state conditions in a suitable engine such as a diesel engine, for instance based on the change in air flow rate through one or more of the fuel injector nozzles as a result of using the fuel composition under test. Conveniently the results are averaged over all of the injector nozzles of the engine. The CEC standard test method F-23-T-00, which involves injector nozzle air flow measurements, may for instance be used to assess engine fouling.

The Fischer-Tropsch derived fuel is preferably included in the fuel composition at a concentration sufficient to achieve a reduction in engine fouling (measured for instance as outlined above) of at least 5 %, preferably at least 8 %, more preferably at least 10 %, most preferably at least 20 %, as compared to that which results from using (under the same or comparable conditions) the same fuel composition but without, or with less of (suitably with 5 % v/v or less of, more suitably 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or from using the same fuel composition prior to replacement, in accordance with the present invention, of some or all of its detergent or other additive(s) by the Fischer-Tropsch derived fuel.

More preferably, the Fischer-Tropsch derived fuel is included at a concentration sufficient to remove, at

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least partially, combustion related deposits which have built up in an engine's fuel injection system, in particular in the injector nozzles, during a previous period of running using another automotive fuel

5 (typically a fuel containing no, or less than 5 % v/v, or less than 1 % w/v, Fischer-Tropsch derived fuels), when the engine is subsequently run on the Fischer-Tropsch fuel containing composition. This concentration is preferably sufficient to remove at least 5 % of the
10 previously incurred injector deposits (measured for instance as described above), more preferably at least 10 %, most preferably at least 15 or 20 or 25 %.

The removal of combustion related deposits may be achieved by running the engine on the Fischer-Tropsch
15 fuel containing composition for instance for the same period of time as that during which the deposits accumulated, or more preferably for 75 %, yet more preferably 50 % or even 40 % or 30 %, of the period of deposit accumulation, conveniently under comparable
20 conditions. Ideally at least partial removal of combustion related deposits is achieved by running the engine on the Fischer-Tropsch fuel containing composition for five hours or less, preferably for three hours or less, more preferably for two hours or less.

25 In practising the present invention, according to either its first or its second aspect, the fuel composition may, in order to achieve the desired purpose(s), consist essentially of the Fischer-Tropsch derived fuel - in other words it may contain a major
30 proportion (by which is meant preferably 99 % v/v or more of the fuel composition, more preferably 99.5 % v/v or more, most preferably 99.8 % v/v or more, even up to 100 %), of the Fischer-Tropsch derived fuel, optionally

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with a minor proportion of one or more suitable fuel additives such as are known in the art (though ideally without antifoaming, dehazing and/or detergent additives), but with no other fuel components present.

5 Alternatively, the fuel composition may contain, in addition to the Fischer-Tropsch derived fuel, one or more other fuel components of conventional type, in particular diesel fuel components such as a diesel base fuel (which may itself comprise a blend of two or more diesel fuel
10 components).

The concentration of the Fischer-Tropsch derived fuel in the composition will be chosen to achieve the desired antifoaming and/or dehazing and/or detergency properties, and may also be influenced by other
15 properties (for example, density, cetane number and/or emissions performance) required of the overall composition.

The concentration of the Fischer-Tropsch derived fuel in the composition is preferably 15 % v/v or
20 greater, more preferably 20 % or 25 % v/v or greater, still more preferably 30 % or 40 % or 50 % v/v or greater. It may be up to 40 % or 50 % or 60 % or 70 % or 80 % or 90 % or 95 % or 98 % v/v of the overall composition. Suitable concentrations might lie, for
25 instance, from 20 to 90 % v/v or from 25 to 80 % v/v or from 25 to 50 % v/v or from 30 to either 70 or 60 or 50 % v/v.

Any additional fuel component(s) in the composition may be fuels of conventional type. They, and ideally
30 also the overall fuel composition, are preferably low or ultra low sulphur fuels, or sulphur free fuels, for instance containing at most 500 ppmw, preferably no more

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than 350 ppmw, most preferably no more than 100 or 50 ppmw, or even 10 ppmw or less, of sulphur.

For use in a diesel fuel composition, for example, typical diesel fuel components may comprise liquid
5 hydrocarbon middle distillate fuel oils, for instance petroleum derived gas oils. They may be organically or synthetically derived, although not Fischer-Tropsch derived. Such fuels will typically have boiling points within the usual diesel range of 150 to 400 °C, depending
10 on grade and use.

When used in a diesel fuel composition, they will typically have densities from 0.75 to 0.9 g/cm³, preferably from 0.8 to 0.86 g/cm³, at 15 °C (eg, ASTM D4502 or IP 365) and cetane numbers (ASTM D613) of from
15 35 to 80, more preferably from 40 to 75. They will typically have initial boiling points in the range 150 to 230 °C and final boiling points in the range 290 to 400 °C. Their kinematic viscosity at 40 °C (ASTM D445) might suitably be from 1.5 to 4.5 centistokes (mm²/s).

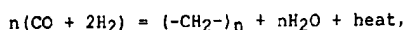
20 The Fischer-Tropsch derived fuel, and any other fuel component(s) present in the composition, will suitably all be in liquid form under ambient conditions.

Where the Fischer-Tropsch derived fuel is a gas oil, it is preferably suitable for use as a diesel fuel. Its
25 components (or the majority, for instance 95 % w/w or greater, thereof) should therefore have boiling points within the typical diesel fuel ("gas oil") range, ie, from about 150 to 400 °C or from 170 to 370 °C. It will suitably have a 90 % w/w distillation temperature of from
30 300 to 370 °C.

By "Fischer-Tropsch derived" is meant that the fuel is, or derives from, a synthesis product of a Fischer-

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Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons :



5 in the presence of an appropriate catalyst and typically at elevated temperatures (eg, 125 to 300 °C, preferably 175 to 250 °C) and/or pressures (eg, 5 to 100 bar, preferably 12 to 50 bar). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

10 The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane.

Gas oil, naphtha and kerosene products may be
15 obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of Fischer-Tropsch synthesis products or from hydrotreated Fischer-Tropsch synthesis products. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, eg,
20 GB-B-2077289 and EP-A-0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to
25 hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that
30 hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

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Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in
5 US-A-4125566 and US-A-4478955.

Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic
10 table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0583836 (pages 3 and 4).

An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in
15 "The Shell Middle Distillate Synthesis Process", van der Burgt et al (*supra*). This process (also sometimes referred to as the Shell™ "Gas-to-Liquids" or "GtL" technology) produces middle distillate range products by conversion of a natural gas (primarily methane) derived
20 synthesis gas into a heavy long chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. A version of the SMDS process, utilising a fixed bed
25 reactor for the catalytic conversion step, is currently in use in Bintulu, Malaysia and its products have been blended with petroleum derived gas oils in commercially available automotive fuels.

Gas oils, naphtha fuels and kerosenes prepared by
30 the SMDS process are commercially available for instance from the Royal Dutch/Shell Group of Companies. Further examples of Fischer-Tropsch derived gas oils are described in EP-A-0583836, EP-A-1101813, WO-A-97/14768,

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WO-A-97/14769, WO-A-00/20534, WO-A-00/20535,
WO-A-00/11116, WO-A-00/11117, WO-A-01/83406,
WO-A-01/83641, WO-A-01/83647, WO-A-01/83648 and
US-A-6204426.

5 Suitably, in accordance with the present invention,
a Fischer-Tropsch derived gas oil will consist of at
least 70 % w/w, preferably at least 80 % w/w, more
preferably at least 90 % w/w, most preferably at least
10 95 % w/w, of paraffinic components, preferably iso- and
linear paraffins. The weight ratio of iso-paraffins to
normal paraffins will suitably be greater than 0.3 and
may be up to 12; suitably it is from 2 to 6. The actual
value for this ratio will be determined, in part, by the
hydroconversion process used to prepare the gas oil from
15 the Fischer-Tropsch synthesis product. Some cyclic
paraffins may also be present.

By virtue of the Fischer-Tropsch process, a Fischer-
Tropsch derived fuel has essentially no, or undetectable
levels of, sulphur and nitrogen. Compounds containing
20 these heteroatoms tend to act as poisons for Fischer-
Tropsch catalysts and are therefore removed from the
synthesis gas feed. This can yield additional benefits,
in terms of effect on catalyst performance, in fuel
compositions prepared in accordance with the present
25 invention.

Further, the Fischer-Tropsch process as usually
operated produces no or virtually no aromatic components.
The aromatics content of a Fischer-Tropsch derived fuel,
suitably determined by ASTM D4629, will typically be
30 below 1 % w/w, preferably below 0.5 % w/w and more
preferably below 0.1 % w/w.

Generally speaking, Fischer-Tropsch derived fuels
have relatively low levels of polar components, in

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particular polar surfactants, for instance compared to petroleum derived fuels. It is believed that this contributes to their improved antifoaming and dehazing performance. Such polar components may include for example oxygenates, and sulphur and nitrogen containing compounds. A low level of sulphur in a Fischer-Tropsch derived fuel is generally indicative of low levels of both oxygenates and nitrogen containing compounds, since all are removed by the same treatment processes.

A Fischer-Tropsch derived gas oil useable in the present invention will typically have a density from 0.76 to 0.79 g/cm³ at 15 °C; a cetane number (ASTM D613) greater than 70, suitably from 74 to 85; a kinematic viscosity (ASTM D445) from 2 to 4.5, preferably 2.5 to 4.0, more preferably from 2.9 to 3.7, centistokes (mm²/s) at 40 °C; and a sulphur content (ASTM D2622) of 5 ppmw or less, preferably of 2 ppmw or less.

Preferably it is a product prepared by a Fischer-Tropsch methane condensation reaction using a hydrogen/carbon monoxide ratio of less than 2.5, preferably less than 1.75, more preferably from 0.4 to 1.5, and ideally using a cobalt containing catalyst. Suitably it will have been obtained from a hydrocracked Fischer-Tropsch synthesis product (for instance as described in GB-B-2077289 and/or EP-A-0147873), or more preferably a product from a two-stage hydroconversion process such as that described in EP-A-0583836 (see above). In the latter case, preferred features of the hydroconversion process may be as disclosed at pages 4 to 6, and in the examples, of EP-A-0583836.

Where the Fischer-Tropsch derived fuel is a naphtha fuel, it will be a liquid hydrocarbon middle distillate

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fuel with a final boiling point of typically up to 220 °C or preferably of 180 °C or less. Its initial boiling point is preferably higher than 25 °C, more preferably higher than 35 °C. Its components (or the majority, for instance 95 % w/w or greater, thereof) are typically hydrocarbons having 5 or more carbon atoms; they are usually paraffinic.

The distillation properties of such a naphtha fuel tend to be comparable to those of gasoline. As with the corresponding gas oils, Fischer-Tropsch derived naphtha fuels tend to be low in undesirable fuel components such as sulphur, nitrogen and aromatics.

In the context of the present invention, a Fischer-Tropsch derived naphtha fuel preferably has a density of from 0.67 to 0.73 g/cm³ at 15 °C and/or a sulphur content of 5 ppmw or less, preferably 2 ppmw or less. It preferably contains 95 % w/w or greater of iso- and normal paraffins, preferably from 20 to 98 % w/w or greater of normal paraffins. It is preferably the product of a SMDS process, preferred features of which may be as described above in connection with Fischer-Tropsch gas oils.

Where the Fischer-Tropsch derived fuel is a kerosene fuel, it will be a liquid hydrocarbon middle distillate fuel with a distillation range suitably from about 150 to 250 °C or from about 150 to 200 °C. It will have a final boiling point of typically from 190 to 260 °C, for instance from 190 to 210 °C for a typical "narrow-cut" kerosene fraction or from 240 to 260 °C for a typical "full-cut" fraction. Its initial boiling point is preferably from 140 to 160 °C. Again, Fischer-Tropsch derived kerosenes tend to be low in undesirable fuel components such as sulphur, nitrogen and aromatics.

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A Fischer-Tropsch derived kerosene fuel preferably has a density of from 0.730 to 0.760 g/cm³ at 15 °C - for instance from 0.730 to 0.745 g/cm³ for a narrow-cut fraction and from 0.735 to 0.760 g/cm³ for a full-cut fraction -, and/or a sulphur content of 5 ppmw or less. It is preferably the product of a SMD3 process, preferred features of which may be as described above in connection with Fischer-Tropsch gas oils.

When practising the present invention, the Fischer-Tropsch derived fuel is conveniently a gas oil as used in Examples 1, 2 and 4 to 6 below, or one having the same or a similar antifoaming and/or dehazing and/or detergency properties and/or the same or a similar density and/or cetane number.

In accordance with the present invention, more than one Fischer-Tropsch derived fuel of the types described above may be used in a fuel composition.

The present invention may be applicable where the fuel composition is suitable for, and/or intended for, use in any system which can be powered by or otherwise consume a fuel, in particular a diesel fuel, composition. In particular it may be suitable, and/or intended, for use in an internal or external (preferably internal) combustion engine, more particularly for use as an automotive fuel and most particularly for use in an internal combustion engine of the compression ignition (diesel) type. Such a diesel engine may be of the direct injection type, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or of the indirect injection type. It may be a heavy or a light duty diesel engine.

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Where the fuel composition is such an automotive diesel fuel composition, it preferably falls within applicable current standard specification(s) such as for example EN 590:99. It suitably has a density from 0.82 to 0.845 g/cm³ at 15 °C; a final boiling point (ASTM D86) of 360 °C or less; a cetane number (ASTM D613) of 51 or greater; a kinematic viscosity (ASTM D445) from 2 to 4.5 centistokes (mm²/s) at 40 °C; a sulphur content (ASTM D2622) of 350 ppmw or less; and/or a total aromatics content (IP 391(mod)) of less than 11.

The fuel composition may be suitable for, and/or intended for, use as an industrial gas oil, for instance for use in a heating or other fuel combustion system.

Generally speaking, and subject to the desire to reduce additive levels by using the Fischer-Tropsch derived fuel, in the context of the present invention any fuel component or fuel composition may be additivated (additive containing) or unadditivated (additive free). Such additives may be added at various stages during the production of a fuel composition; in the case of automotive fuels those added to a base fuel at the refinery for example might be selected from anti-static agents, pipeline drag reducers, flow improvers (eg, ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers) and wax anti-settling agents (eg, those commercially available under the Trade Marks "PARAFLOW" (eg, PARAFLOW™ 450, ex Infineum), "OCTEL" (eg, OCTEL™ W 5000, ex Octel) and "DODIFLOW" (eg, DODIFLOW™ v 3958, ex Hoechst).

Thus if the fuel composition contains additives, they will typically although not necessarily be incorporated together with one or more of the constituent

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fuel components (including the Fischer-Tropsch derived component), whether at or downstream of the refinery. Suitably however the composition will contain only a minor proportion (preferably less than 1 % w/w, more preferably less than 0.5 % w/w (5000 ppmw) and most preferably less than 0.2 % w/w (2000 ppmw)) of any such fuel additives.

Components which may be incorporated in fuel additives, in particular for use in diesel fuels, include lubricity enhancers such as EC 832 and PARADYNE™ 655 (ex Infineum), HITEC™ E580 (ex Ethyl Corporation) and VEKTRON™ 6010 (ex Infineum) and amide based additives such as those available from the Lubrizol Chemical Company, for instance LZ 539 C; ignition improvers (cetane improvers) (eg, 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US-A-4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (eg, that sold commercially by Rhein Chemie, Mannheim, Germany as "RC 4801", a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, eg, the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (eg, phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); and metal deactivators.

Where, in practising the present invention, the fuel composition contains any additives at all, and in particular when it is a diesel fuel composition, it may

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be particularly preferred for it to include at least a lubricity enhancer, especially when the composition has a low (eg, 500 ppmw or less) sulphur content. Any such lubricity enhancer is conveniently present at a concentration from 50 to 1000 ppmw, preferably from 100 to 1000 ppmw, based on the overall fuel composition.

The (active matter) concentration of any ignition improver present will preferably be 600 ppmw or less, more preferably 500 ppmw or less, conveniently from 300 to 500 ppmw.

Unless otherwise stated, and again subject to the desire to reduce additive levels by using the Fischer-Tropsch derived fuel, the (active matter) concentration of any other type of additive in the overall fuel composition is preferably up to 1 % w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

According to a third aspect of the present invention, there is provided the use of a Fischer-Tropsch derived fuel, and/or of a fuel composition containing it, to reduce loss of efficiency of fuel atomisation and/or combustion in a fuel consuming system which is running on, or is to be run on, the fuel or composition. "Fuel consuming" includes fuel powered.

A fourth aspect provides the use of a Fischer-Tropsch derived fuel, and/or of a fuel composition containing it, to reduce build up of deposits, in particular silicon deposits, in a fuel consuming system which is running on, or is to be run on, the fuel or composition.

According to the third and fourth aspects of the present invention, "use" of the fuel or fuel composition includes introducing it into the system and suitably also

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operating the system using the fuel or composition.

"Use" of a Fischer-Tropsch derived fuel in this context may involve incorporating it into a fuel composition, typically as a blend (ie, a physical mixture) with one or
5 more other fuel components and/or fuel additives, introducing the composition into the fuel consuming system and suitably also operating the system using the fuel composition. Alternatively, the use may involve introducing the Fischer-Tropsch derived fuel alone into
10 the system, and suitably also operating the system using it.

In the context of the third and fourth aspects, the fuel consuming system is preferably, or is part of, a combustion system, in particular comprising an internal
15 combustion engine for an automotive vehicle, such as a diesel engine; it may in particular be a fuel injection system within such a combustion system. The deposits in question are likely to build up in its fuel injection system such as in and around the injector nozzles.

20 Efficiency of fuel atomisation and/or combustion in a fuel powered (typically fuel combustion) system may be assessed with reference to the efficiency of fluid flow through the atomisation nozzle(s), for instance as described above in connection with injector fouling. Any
25 deposits accumulated in the nozzle(s) will reduce the area through which fluid can flow and hence the atomisation and combustion efficiency. A suitable method for measuring air flow through fuel injector nozzles is ISO 4010-1977.

30 A reduction in fuel atomisation and/or combustion efficiency may also be manifested by a loss of power output, and/or by an increase in undesirable emissions,

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from the system, for instance in a vehicle driven by a combustion engine.

Preferred degrees of reduction in atomisation and combustion efficiency may be as described in connection with nozzle fouling in the context of the first and second aspects of the present invention.

Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve, and/or in a context suitable for achieving, a reduction in fuel atomisation and/or combustion efficiency which is at least 2 % lower than, more preferably at least 5 % or 8 % or 10 % lower than, that caused over the same time period and under the same test conditions by running the system on a non-Fischer-Tropsch derived fuel, and/or by running the system on the same fuel composition but without, or with less of (suitably 5 % v/v or less of, more suitably 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or by running the system on the same fuel composition prior to replacement, in accordance with the present invention, of some or all of its antifoaming, dehazing, detergent and/or other additive(s) by the Fischer-Tropsch derived fuel.

Levels of deposits in a fuel consuming system may be assessed for instance using a scanning electron microscope, and/or by X-ray or other spectroscopic analysis of components of the system (in particular fuel injector nozzles), over a period of running the system on the fuel or fuel composition in question.

Preferably the Fischer-Tropsch derived fuel is used in an amount sufficient to achieve, and/or in a context suitable for achieving, a reduction in the level of silicon deposits caused over the same time period and under the same test conditions by running the system on a

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non-Fischer-Tropsch derived fuel, and/or by running the system on the same fuel composition but without, or with less of (suitably 5 % v/v or less of, more suitably 1 % v/v or less of), the Fischer-Tropsch derived fuel present, and/or by running the system on the same fuel composition prior to replacement, in accordance with the present invention, of some or all of its antifoaming, dehazing, detergent and/or other additive(s) by the Fischer-Tropsch derived fuel.

Preferably it is used in an amount and/or context sufficient to achieve no or only negligible silicon deposits in a fuel injection system running on the fuel or composition.

The reduction may be assessed over any appropriate test period, for instance 10 operating hours or more, suitably 100 or 200 or 500 operating hours or more. It may be assessed over the lifetime or expected lifetime of the system, for instance up to 5,000 operating hours for a typical passenger vehicle or up to 50,000 operating hours for a commercial vehicle or a stationary generator.

According to a fifth aspect of the present invention, there is provided a method of operating a fuel consuming system, which method involves introducing into the system, preferably into a combustion chamber of the system, a fuel composition containing a Fischer-Tropsch derived fuel, for one or more of the purposes described above in connection with the first to the fourth aspects of the present invention. The system again suitably comprises an internal or external combustion engine, more preferably the former, most preferably a diesel engine.

The fifth aspect of the present invention encompasses a method of operating a machine which is powered by a fuel combustion system, especially a vehicle

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which is driven by a combustion engine, in particular a diesel powered vehicle.

Preferred features of the third to the fifth aspects of the present invention, in particular as regards the nature and concentration of the Fischer-Tropsch derived fuel and of any other fuel components and additives present in the fuel composition, and as regards the extent to which any intended purpose is achieved, may be as described above in connection with the first and second aspects of the present invention.

A sixth aspect of the present invention provides a process for the preparation of a fuel composition, which process involves blending a Fischer-Tropsch derived fuel with one or more other fuel components and/or with one or more fuel additives. The blending is ideally carried out for one or more of the purposes described in connection with the first to the fifth aspects of the present invention, either in relation to the properties of the fuel composition and/or to its effect on a fuel consuming system into which it is or is intended to be introduced.

Again, preferred features of this sixth aspect of the present invention, in particular regarding the natures and relative proportions of components of the blend (including fuel additives where present) may be as described above in connection with the first to the fifth aspects.

According to a seventh aspect, the present invention provides a fuel composition, in particular an automotive fuel composition such as a diesel fuel composition, comprising either :

- i) a Fischer-Tropsch derived fuel and a silicon free or substantially silicon free antifoaming additive, optionally together with one or more other fuel

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components, the composition preferably being free of detergent additives;

- ii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of antifoaming additives and/or of silicon containing (in particular silicone based) antifoaming additives and/or of dehazing additives, and is preferably also free of detergent additives; or
- 10 iii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of dehazing additives; or
- iv) a Fischer-Tropsch derived fuel and one or more non-detergent fuel additives, optionally together with one or more other fuel components, wherein the composition is free of or substantially free of silicon.

The natures and concentrations of fuel additives and additional fuel components, where present, may be as described above in connection with the first to the sixth aspects of the present invention. In the case of options (ii) and (iii), for example, the one or more non-detergent fuel additives may be selected from the group consisting of antifoaming additives, dehazing additives, lubricity enhancers, ignition improvers, anti-rust agents, corrosion inhibitors, reodorants, anti-wear additives, anti-oxidants, metal deactivators, anti-static agents, pipeline drag reducers, flow improvers, wax anti-settling agents and mixtures thereof. They might typically be diesel fuel additives. They will not generally be oxygenates (ie, oxygen containing compounds, in particular materials containing groups such as -OH or C=O or -O- or -C(O)O-, which are added to increase the

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oxygen content of a fuel). In cases they will not include diesel fuel ignition improvers, such as organic nitrates and/or nitrites.

5 In the context of silicon content, "substantially free" is intended to encompass 50 ppbw or less silicon, preferably 20 or 10 ppbw or less.

Where a composition according to the seventh aspect of the present invention is to be free of a given additive type, it may alternatively contain only low
10 levels of the relevant additive. In the case of antifoaming additives, a low level may be for example 300 ppmw or less, preferably 200 or 100 ppmw or less. In the case of dehazing additives, a low level may be for example 10 ppmw or less, preferably 5 ppmw or less. In
15 the case of detergent additives, a low level may be for example 100 ppmw or less, preferably 50 or 20 ppmw or less.

A composition according to the seventh aspect of the present invention may be prepared using a process
20 according to the sixth, and/or used in the ways described in connection with the first to the fifth aspects.

An eighth aspect of the present invention provides a method of operating a fuel consuming system, the method involving introducing into the system, and preferably
25 running the system on, a fuel composition according to the seventh aspect.

A ninth aspect provides a method of operating a fuel consuming system, in particular an internal combustion engine such as a diesel engine, the method involving
30 introducing into the system, and preferably running the system on, a fuel composition prepared by putting any of the first to the sixth aspects of the present invention into effect. Such a fuel composition is preferably free

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of antifoaming and/or silicon containing and/or dehazing additives, more preferably is also free of detergent additives, and yet more preferably is completely free of additives. In the case of each type of additive, the composition may instead of being free of the relevant additive contain only low levels of it, as described in connection with the seventh aspect of the present invention. The composition is preferably free or substantially free of silicon.

Other preferred features of the seventh, eighth and ninth aspects of the present invention may be as described in connection with the first to the sixth aspects.

According to a tenth aspect of the present invention, there is provided the use, in a fuel or fuel composition, of a reduced level of silicon, for the purpose of :

- (a) reducing loss of efficiency of fuel atomisation and/or combustion in a fuel consuming system which is running on, or is to be run on, the fuel or composition; and/or
- (b) reducing build up of deposits, in particular silicon deposits, in a fuel consuming system which is running on, or is to be run on, the fuel or composition.

In this context "use" of a particular level of silicon includes preparing a fuel composition with that level of silicon in it (which may include removing silicon or silicon containing components from the composition), and/or running a fuel consuming system using such a fuel composition.

A reduced level of silicon may be as compared to the level of silicon which would otherwise have been incorporated into the fuel composition in order to

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achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the level of silicon which was present in the fuel composition prior to the realisation
5 that silicon levels could be reduced in order to achieve the effects (a) and/or (b) provided by the present invention, and/or which was present in an otherwise analogous fuel composition intended (eg, marketed) for use in an analogous context.

10 The reduced level is preferably achieved by reducing the concentration of additive(s), in particular antifoaming additive(s), in the fuel composition. A "reduced level" encompasses no or substantially no silicon at all.

15 Other preferred features of the tenth aspect of the present invention, for instance regarding the nature and uses of the fuel composition and the fuel consuming system, and as regards the extent to which any intended purpose is achieved, may be as described above in
20 connection with the first to the ninth aspects.

The present invention will be further understood from the following examples, which illustrate the antifoaming and dehazing effects of a Fischer-Tropsch derived fuel, both alone and in blends with conventional
25 petroleum derived fuels, and the potential uses of such properties in fuel systems and in particular in diesel engines.

Example 1

30 A Fischer-Tropsch (SMDS) derived gas oil fuel F1 was blended in various proportions with a conventional petroleum derived ultra low sulphur diesel fuel F2, and the antifoaming properties assessed for the blends as well as for the neat fuels F1 and F2.

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Both fuels were commercially available and were sourced from the Royal Dutch/Shell Group of Companies. Their properties are shown in Table A.

Table A

Fuel property	Test method	F1	F2
Density @ 15°C (g/cm ³)	IP 365/ASTM D4052	0.7352	0.8328
Distillation	IP 123/ASTM D86		
IBP (°C)		211.5	169.0
10%		249.0	209.0
20%		262.0	231.0
30%		274.0	249.0
40%		286.0	262.5
50%		298.0	274.5
60%		307.5	285.5
70%		317.0	296.5
80%		326.5	309.0
90%		339.0	327.0
95%		349.0	342.0
FBP		354.5	357.0
Cetane number	ASTM D613	>74.8	54.8
Cetane index	IP 364/84/ASTM D976	77.2	54.6
Kinematic viscosity @ 40 °C (centistokes) (mm ² /s)	IP 71/ASTM D445	3.606	
Cloud point (°C)	IP 219	+2	-7
Sulphur (WDXRF) (ppmw)	ASTM D2622	<5	38
HPLC aromatics (%w/w):	IP 391 (mod)		
Mono		0.1	19
Di		<0.1	3.3
Tri		<0.1	0.5
Total		0.1	22.8

The gas oil F1 had been obtained from a Fischer-Tropsch (SMDS) synthesis product via a two-stage hydroconversion process analogous to that described in EP-A-0583836.

Antifoaming performance for each fuel or blend was assessed using a test procedure based on the Association

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Français de Normalisation (AFNOR) procedure NF M 07-075. A 100 ml sample of the fuel or blend was pumped under controlled conditions into a measuring cylinder, as laid down in NF M 07-075, and the volume of foam produced was measured. The foam was then allowed to collapse and its dissipation time recorded.

The results are shown in Table 1.

Table 1

Experiment no.	Volume % F1	Volume % F2	Foam volume (ml)	Dissipation time (s)
1.1	0 (ie, fuel F2 alone)	100	107	41
1.2	10	90	108	41
1.3	30	70	104	33
1.4	50	50	102	33
1.5	70	30	94	25
1.6	90	10	84	22
1.7	100	0 (ie, fuel F1 alone)	82	14

It can be seen that incorporation of the Fischer-Tropsch derived fuel F1 gives a significant antifoaming benefit compared to the performance of the petroleum derived diesel fuel F2 alone, in particular in terms of reduced foam dissipation times. The antifoaming performance of F1 is markedly superior to that of F2.

Example 2

The antifoaming performance of F1 was compared with that of other commercially available, petroleum derived diesel fuels F3 to F7. The properties of these fuels are summarised in Table B; they were selected to represent a range of different diesel fuel qualities. F3, F4, F5 and F7 were sourced via the Royal Dutch/Shell Group of

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Companies. F6 was sourced in Argentina to correspond to that country's typical production quality.

Table B

Fuel property	Test method	F3	F4	F5	F6	F7
Geographical origin		Germany	France	Turkey	Argentina	Germany
Density @ 15°C (g/cm ³)	IP 365/ ASTM D4052	0.8403	0.8348	0.8334	0.8377	0.8477
Distillation	IP 123/ ASTM D86					
IBP (°C)		180.0	173.5	188.0	184.5	198.0
10%		220.0	203.1	221.5	222.0	238.5
20%		237.0	221.8	237.5	240.5	254.5
30%		251.5	239.6	250.5	259.0	266.0
40%		264.0	255.3	263.5	275.0	276.0
50%		276.0	270.2	275.5	290.5	286.0
60%		288.0	284.6	288.5	305.5	296.5
70%		301.0	300.5	301.0	321.0	308.5
80%		316.5	318.6	316.5	339.0	323.5
90%		338.0	340.9	335.5	363.5	346.0
95%		355.0	359.9	351.0	383.5	364.5
FBP		364.5	367.4	362.0	388.0	377.0
Cetane number	ASTM D613	52.9		55.5	59.5	51.1
Cetane index	IP 364/84	52.3	53.0	54.6	55.8	51.7
Kinematic viscosity @ 40 °C (centistokes) (mm ² /s)	IP 71/ ASTM D445	3.020	2.660	3.2	3.9	3.608
Cloud point (°C)	IP 219	-9		-4	4	0
Sulphur (NDXRF) (ppmw)	ASTM D2622	280	269	4200	479	412

5 The antifoaming performance of each of these fuels was tested in the same way as in Example 1, and the performance of F1 also re-tested. The results are shown in Table 2.

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Table 2

Experiment no.	Fuel	Foam volume (ml)	Dissipation time (s)
2.1	F1	81	13
2.2	F2	107	41
2.3	F3	111	59
2.4	F4	109	45
2.5	F5	105	27
2.6	F6	88	58
2.7	F7	87	60

The Fischer-Tropsch derived fuel F1 clearly out-
performs all the other commercially available petroleum
5 derived diesel fuels in the context of antifoaming
properties, both in terms of initial foam volumes and
more particularly foam dissipation rates. Moreover
Example 1 showed that the incorporation of as little as
30 % v/v of F1 into a petroleum derived diesel base fuel
10 can lead to a significant improvement in the antifoaming
performance of the blend compared to that of the base
fuel alone.

Thus, in accordance with the present invention, a
Fischer-Tropsch derived fuel component may be used at
15 least partly to replace a conventional antifoaming
additive in a diesel fuel composition, potentially making
possible compositions which are completely free of
antifoaming agents and yet still have acceptable overall
antifoaming performance. This could also make possible
20 fuel compositions with reduced if not zero or negligible
silicon contents, with the benefits explained in
connection with Example 3 below.

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Moreover these results indicate the potential for using a Fischer-Tropsch derived gas oil as a diesel fuel in its own right, again with reduced if any levels of additives and in particular antifoaming additives, and again without unacceptably poor antifoaming properties.

Example 3

The potential effect of silicone based antifoaming agents in diesel fuel compositions was observed on a diesel engine.

The fuel injectors of a Volvo™ D16A diesel engine were examined under a scanning electron microscope (SEM) following a period of normal use running on standard commercially available (UK) diesel fuels. Such fuels are highly likely to contain silicone based antifoaming additives.

Silicon deposits were detected in the small holes of the fuel injectors, as confirmed both by SEM photographs and also by X-ray analysis of the injector surfaces performed at the same time. The basic constitution of the injector metal, in regions unaffected by fuel contact, showed a silicon content of 0.34 % w/w. At the outer end of the nozzle spray hole, in contrast, the silicon content was 8.16 % w/w, indicating significant deposits of the element which at these levels are postulated to derive from fuel additives passing through the injectors as well as simple environmental pollution (dust, sand and the like).

It is possible that such deposits could contribute, certainly over an extended period of use, to a reduction in fuel atomisation and/or combustion efficiency. As the trend towards increasingly smaller fuel injection holes continues in engines of this type, the build up of such deposits may become a more significant problem. Thus,

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particularly in automotive diesel engines but also in any fuel powered systems comprising fuel injection systems, it would be desirable to be able to use fuels with reduced silicon contents, preferably silicon free.

- 5 Examples 1 and 2 demonstrate that the present invention may be used to provide such fuels, by using a Fischer-Tropsch derived fuel at least partially to replace conventional silicon containing additives.

Example 4

- 10 The Fischer-Tropsch derived gas oil F1 was blended in various proportions with the petroleum derived diesel base fuel F2, and the dehazing performance assessed for the blends as well as for the neat fuels F1 and F2.

- The dehazing test procedure used was based on the
15 ASTM procedure D1094 ("Water reaction of aviation fuels"), but with certain modifications for use with diesel engine fuels. An 80 ml sample of fuel was mixed with 20 ml of an aqueous buffer solution in a measuring cylinder, shaken vigorously and allowed to stand under
20 controlled conditions. The water separated out at the bottom of the sample and the diesel, interface and aqueous layers were then visually rated by their appearance. Volume of loss from the aqueous layer was also visually assessed.

- 25 Although sample preparation was identical to that in the ASTM method, the settling time was increased to 4 hours and the rating procedure was modified to recognise six rather than four degrees of hazing (clouding). In addition, the fuel and water layers were rated separately
30 instead of together as in the ASTM method.

Following visual assessment in this way, the top 50 ml of the fuel layer was drawn from each sample by pipette and its remaining water content assessed using a

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Karl Fischer meter; this allowed further discrimination between samples having the same visual rating scores.

The results are shown in Table 3.

Table 3

Exp ¹ no.	Vol % F1	Vol % F2	Visual ratings : Interface	Fuel layer	Water layer	Water loss (ml)	Water content (mg/kg)
4.1	0 (ie, F2 alone)	100	0	2	1	0	105
4.2	25	75	0	2	1	0.5	95
4.3	50	50	0	1.5	1	0	80
4.4	100	0 (ie, F1 alone)	0	1	1	0	30

5

The visual ratings given in columns 4 to 6 and the water loss figures in column 7 were measured after 4 hours' settling time; the water contents in column 8 were recorded after 24 hours. For the visual ratings, a lower score indicates better performance.

10

The Table 3 data show that the Fischer-Tropsch derived fuel F1 has superior dehazing performance to that of the petroleum derived fuel F2, and can also improve the dehazing performance of F2 when blended with it. The water content after 24 hours' settling is the most sensitive measure of dehazing performance, and in this experiment clearly indicates the superiority of F1 over F2.

15

Example 5

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Example 4 was repeated but comparing F1 with the petroleum derived fuel F4 described in connection with Example 2.

The dehazing results are shown in Table 4, using the same format as for the Table 3 data.

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Table 4

Exp ^t no.	Vol % F1	Vol % F4	Visual ratings : Interface	Fuel layer	Water layer	Water loss (ml)	Water content (mg/kg)
5.1	0 (ie, F4 alone)	100	1	2	1	0.5	140
5.2	50	50	1	2	1	0	115
5.3*	100	0 (ie, F1 alone)	0	1	1	0	30

* Results taken from Example 4.4.

Again, the dehazing performance of F1 was far better than that of F4, and blending F1 with F4 resulted in an improvement in the dehazing performance of the base fuel.

Example 6

The dehazing performance of F1 was compared, using the method of Examples 4 and 5, with those of the diesel base fuels F3 to F7 tested in Example 2. The results are shown in Table 5.

Table 5

Exp ^t no.	Fuel	Visual ratings : Interface	Fuel layer	Water layer	Water loss (ml)	Water content (mg/kg)
6.1*	F1	0	1	1	0	30
6.2	F3	2.5	2	1	1	80
6.3*	F4	1	2	1	0.5	140
6.4	F5	1	2	1	0.5	145
6.5	F6	2	2	1	1.25	80
6.6	F7	1	2	1	0	85

* Results taken from Examples 4 and 5.

Again the Fischer-Tropsch derived fuel F1 outperforms the other diesel fuels, in particular with respect to their 24 hour residual water contents. The Fischer-Tropsch fuel F1 alone has excellent dehazing (water shedding) properties, even in the absence of

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dehazing additives, and is thus potentially useable as an additive free, or at least a dehazer free fuel, or as a low additive fuel. It also has potential for use as a dehazing additive in its own right, when blended with
5 other fuels having inferior dehazing properties - again such blends may contain low levels of, or be free of, additives and in particular dehazing additives, the Fischer-Tropsch fuel in effect replacing some or all of the conventional dehazing additives that might otherwise
10 be needed to lend acceptable dehazing performance to the base fuel(s).

Examples 1, 2 and 4 to 6 together demonstrate the antifoaming and dehazing properties of Fischer-Tropsch derived fuels. These dual effects make such fuels
15 suitable for replacing both types of additives, thus potentially yielding fuel compositions with low overall additive levels, possibly completely additive free, or at least with low levels of - preferably free of - antifoaming and dehazing additives.

Fischer-Tropsch derived fuels, in particular gas oils, have also been found to have detergency properties, and to be of use in diesel fuel compositions for reducing combustion related deposits in engines into which the compositions are introduced and/or for removing
25 previously incurred engine deposits. In other words, they have been shown to be of use in maintaining and even in improving engine cleanliness, by contributing to a reduction in, and/or a reversal of, fuel injector fouling. For these reasons, a Fischer-Tropsch derived
30 fuel, or a fuel composition containing it, can additionally contain reduced if any levels of detergent additives, again raising the possibility of completely or

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substantially additive free fuel compositions based on the present invention.

Moreover the need for reduced detergent levels in compositions containing Fischer-Tropsch fuel components
5 may also give the opportunity for the use of silicon free antifoaming additives, with the associated benefits of lower overall silicon levels and hence reduced engine fouling. Again there is potential for completely silicon free fuel compositions.

The claims defining the invention are as follows:

1. Use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of reducing the amount of additives (other than detergent additives) in the composition.
2. Use according to claim 1, wherein the Fischer-Tropsch derived fuel is used for the purpose of reducing the amount of antifoaming and/or dehazing additives in the composition.
3. Use according to claim 1 or claim 2, wherein the Fischer-Tropsch derived fuel is also used for the purpose of reducing the amount of detergent additives in the composition.
4. Use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of reducing the amount of silicon in the composition.
5. Use of a Fischer-Tropsch derived fuel in a fuel composition, for the purpose of improving the antifoaming and/or dehazing properties of the composition.
6. Use according to any one of the preceding claims, wherein the composition in which the Fischer-Tropsch derived fuel has been used contains no antifoaming additives.
7. Use according to any one of the preceding claims, wherein the composition in which the Fischer-Tropsch derived fuel has been used further comprises a low sulphur, an ultra low sulphur or a sulphur free conventional fuel.
8. Use according to any one of the preceding claims, wherein the Fischer-Tropsch derived fuel is used in the fuel composition at a concentration of 15% v/v or more.
9. Use according to claim 8 wherein the Fischer-Tropsch derived fuel is used in the fuel composition at a concentration of from 20 to 90% v/v, or from 25 to 80% v/v or from 25 to 50% v/v.
10. Use according to any one of the preceding claims, wherein the Fischer-Tropsch derived fuel is a gas oil.
11. Use according to claim 9 wherein the gas oil is suitable for use as a diesel fuel.
12. Use according to any one of the preceding claims, wherein the fuel composition is a diesel fuel composition.

13. A fuel composition comprising either:

(i) a Fischer-Tropsch derived fuel and a silicon free or substantially silicon free antifoaming additive, optionally together with one or more other fuel components, wherein the amount of said antifoaming additive present is less than a fuel composition without said Fischer-Tropsch derived fuel, the composition preferably being free of detergent additives; or

(ii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of antifoaming additives and/or of silicon containing antifoaming additives and/or of dehazing additives, and is preferably also free of detergent additives and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel; or

(iii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of dehazing additives and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel; or

(iv) a Fischer-Tropsch derived fuel and one or more non-detergent fuel additives, optionally together with one or more other fuel components, wherein the composition is free of or substantially free of silicon and substantially free of antifoaming additive and wherein the amount of said antifoaming additive, if present, is less than a fuel composition without said Fischer-Tropsch derived fuel.

14. A process for the preparation of a fuel composition, which process comprises blending either:

(i) a Fischer-Tropsch derived fuel and a silicon free or substantially silicon free antifoaming additive, optionally together with one or more other fuel components, the composition preferably being free of detergent additives; or

(ii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of antifoaming additives and/or of silicon containing antifoaming additives and/or of dehazing additives, and is preferably also free of detergent additives; or

(iii) a Fischer-Tropsch derived fuel and one or more (suitably non-detergent) fuel additives, optionally together with one or more other fuel components, wherein the composition is free of dehazing additives; or

(iv) a Fischer-Tropsch derived fuel and one or more non-detergent fuel additives, optionally together with one or more other fuel components, wherein the composition is free of or substantially free of silicon;

wherein said Fischer-Tropsch fuel is blended for the purpose of reducing the amount of additives (other than detergent additives) in the fuel composition, or for the purpose of reducing the amount of silicon in the fuel composition or for the purpose of improving the antifoaming and/or dehazing properties of the composition.

5 15. A process for the preparation of a fuel composition according to claim 11 wherein said additives (other than detergent additives) are antifoaming additives and/or dehazing additives.

16. Use of a Fischer-Tropsch derived fuel in a fuel composition as defined in claim 1 and substantially as herein described with reference to any one of Examples 1 to 6.

10 17. Use of a Fischer-Tropsch derived fuel in a fuel composition as defined in claim 4 and substantially as herein described with reference to Examples 1, 2 or 3.

18. Use of a Fischer-Tropsch derived fuel in a fuel composition as defined in claim 5 and substantially as herein described with reference to Examples 1, 2, 4, 5 or 6.

19. A fuel composition as defined in claim 10 and substantially as herein described with reference to any one of Examples 1 to 6.

15 20. A process of preparing a fuel composition as defined in claim 10 which process is substantially as herein described with reference to any one of Examples 1, 4 and 5.

Dated 16 October, 2008

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